

## PATENT ABSTRACTS OF JAPAN

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(54) OPTICALLY TRANSMITTING RARE EARTH-ALUMINUM GARNET SINTERED PRODUCT  
AND PRODUCTION METHOD THEREFOR

(57)Abstract:

PROBLEM TO BE SOLVED: To provide optically transmitting rare earth-aluminum garnet sintered product that has high light straight transmittance and high mechanical strength.

SOLUTION: This optically transmitting rare earth-aluminum garnet sintered product has a void volume of  $\leq 100$  vol. ppm; the molar ratio of rear earths/Al of  $0.599 \leq R/Al \leq 0.601$ ; Si  $\leq 15$  wt.ppm in  $0.599 \leq R/Al \leq 0.600$ ; and Si (wtppm)  $\leq 15000 \times (R/Al) - 8985$  in  $0.600 \leq R/Al \leq 0.601$ .

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CLAIMS

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[Claim(s)]

[Claim 1] The translucency rare earth aluminum garnet sintered compact which it is the sintered compact which has the garnet structure where the crystal structure is expressed with general formula  $R_3\text{aluminum}_5\text{O}_{12}$  (R is any one sort of rare earth elements among Y, Dy, Ho, Er, Tm, Yb, and Lu), and the pore in a sintered compact is 100 or less volppms, and is brought into an infrared region and characterized by optical straight-line permeability other than unique absorption wavelength being 83% or more by 5mm thickness since visible.

[Claim 2] The translucency rare earth aluminum garnet sintered compact of claim 1 which the ratio of rare earth elements and aluminum is  $0.599 \leq R/\text{aluminum} \leq 0.601$  in mol conversion, and Si in a sintered compact is [ the ratio of rare earth elements and aluminum ] 15 or less wtppms in  $0.599 \leq R/\text{aluminum} \leq 0.600$ , and is characterized by what the ratio of rare earth elements and aluminum is [ Si in a sintered compact ]  $\text{Si}(\text{wtppm}) \leq 15000 \times (R/\text{aluminum}) - 8985$  in  $0.600 < R/\text{aluminum} \leq 0.601$ .

[Claim 3] The primary ceramic Plastic solid expressed with general formula  $R_3\text{aluminum}_5\text{O}_{12}$  (R is any one sort of rare earth elements among Y, Dy, Ho, Er, Tm, Yb, and Lu) by which the floc to which specific surface area exceeds 3 micrometers by  $3-15\text{m}^2/\text{g}$  was produced using 5% or less of raw material powder with the weight fraction is calcinated. the mean particle diameter of 3 micrometers or less, and a theoretical density ratio -- the pore in a sintered compact by 100 or less volppms by making eburnation 94% or more and giving isotropic pressure pressurization between heat to this primary sintered compact The manufacture approach of the translucency rare earth aluminum garnet sintered compact characterized by crossing to an infrared region and optical straight-line permeability other than unique absorption wavelength considering as 83% or more of sintered compact by 5mm thickness since visible.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Application of the Invention] This invention relates to the translucency sintered compact which has the garnet structure expressed with general formula  $R_3\text{aluminum } 5O_{12}$  (R is any one sort of rare earth elements among Y, Dy, Ho, Er, Tm, Yb, and Lu), and its manufacture approach. The sintered compact of this invention is used suitable for anticorrosion members, such as for example, sapphire alternative aperture material, a polarizing plate, an envelope for discharge lamps, and semiconductor fabrication machines and equipment, accessories, etc.

[0002]

[Description of the Prior Art] The crystal structure is a cubic, and since the sintered compact excellent in translucency or thermal resistance is obtained, the rare earth aluminum garnet compound expressed with general formula  $R_3\text{aluminum } 5O_{12}$  (R is any one sort of rare earth elements among Y, Dy, Ho, Er, Tm, Yb, and Lu) can perform application for various applications. Though it is the polycrystalline substance by removing completely especially the pore and the unusual appearance which are the scattering source of light, since the transparency which is equal to a single crystal is acquired, application to various optical materials is expected.

[0003] Especially, in order that the yttrium aluminum garnet ( $Y_3\text{aluminum } 5O_{12}:\text{YAG}$ ) ceramics may show the translucency which was excellent over the large area from a visible region to an infrared region, the reinforcement, the thermal resistance, and the configuration degree of freedom which are the advantage of the ceramics are expected, and the application to sapphire alternative aperture material, the luminescence tubing for discharge lamps, an anticorrosion member, etc. is considered. On the other hand, since the translucency rare earth aluminum garnet sintered compact using rare earth elements other than an yttrium cannot find out that rare earth elements are comparatively expensive and a further specific application, although it is the same as that of the case where manufacture conditions are YAG ceramics, almost, a report of the manufacture approach is hardly found.

[0004] As the manufacture approach of the translucency YAG ceramics that research is done more briskly than before, what is depended on hot pressing (United States patent : 3767 745), the direct sintering method (JP, 3-218963, A) by ball mill mixing and CIP shaping of oxide impalpable powder, etc. are learned. Hot pressing makes difficult manufacture of the complicated configuration article which is one of the descriptions of the ceramics. In oxide impalpable powder alligation, in order to control the separation of yttria and an alumina based on the specific gravity difference at the time of mixing while increasing reactivity although the good sintered compact of translucency is obtained, the superfines object of yttria is used. For this reason, when it is necessary to manufacture yttria and an alumina separately, in order to use a superfines object, there is an inclination for a shaping consistency to become low. If a shaping consistency is low, the contraction at the time of sintering is large, and application is difficult for the application as which dimensional accuracy is required. In order to obtain the sintered compact in which still more sufficient translucency is shown, it is necessary to add

SiO<sub>2</sub> as sintering acid and to perform baking for dozens hours. Moreover, although the method (JP,2-92817,A) of obtaining a translucency sintered compact using single phase YAG impalpable powder is also indicated, since the degree of sintering of raw material powder is scarce, the sintering acid of SiO<sub>2</sub> grade is needed.

[0005] The scattering sources of the light in the ceramics with which the crystal structure generally consists of a cubic are pore and an unusual appearance, and in order to obtain the sintered compact excellent in translucency, they need to remove these completely. In the oxide of the two-component system like a rare earth aluminum garnet sintered compact, generating of an unusual appearance can be controlled by controlling a presentation strictly. Since it not only reduces translucency, but the source of destruction can change, existence of pore is not desirable. Therefore, in order to excel in translucency and to obtain a reliable sintered compact also mechanically, it becomes a technical problem how pore is removed.

[0006] In the conventional method, eburation and a grain growth rate are controlled by sintering acid and baking conditions, and pore is discharged through the grain boundary by the volume diffusion by grain growth. However, by manufacture of the ceramics using usual raw material powder and a usual mechanical-molding method, uniform packing of a raw material particle is impossible, and the hole of the magnitude which cannot be removed produces it in the usual sintering to some extent. Therefore, it is difficult to obtain the polycrystalline substance which the pore of several 100 or more volppms remains inside a sintered compact, and the translucent ceramics generally called precise object also show the same optical property as a single crystal. For example, it reports that pore is recognizing 150volppm existence also at the lowest to the interior of the Nd addition YAG ceramics obtained by the vacuum sintering process, and it has very many these values jar NARUOBU material science (Journal of Materials Science) 34 (1999) 1189-1195 as compared with it of a single crystal.

[0007] By the way, in production of translucent alumina, it is indicated that the sintered compact which does not contain pore is obtained by the isotropic pressure pressurization between heat (Hot Isostatic Press:HIP) (JP,8-301666,A). In HIP, two or more hundreds kgf/cm high pressure is applied to a sample isotropic under an elevated temperature, and plastic deformation removes the pore in the ceramics. On the other hand, HIP is applied to the YAG ceramics, and journal OBUAMERIKAN ceramic society (J. Am.Ceram.Soc) 79[7]1927-33 (1996) is reported as an example which was going to produce the non-pore sintered compact. However, in this report, since Ar gas which is a pressure medium remains as pore inside a sintered compact, it is made impossible to produce a non-pore YAG sintered compact. As stated above, the non-pore sintered compact of rare earth aluminum garnets including YAG is not known for the conventional method.

[0008]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the rare earth aluminum garnet sintered compact excellent in light transmittance, and its manufacture approach.

[0009]

[Elements of the Invention] It is the sintered compact which has the garnet structure where the crystal structure is expressed with general formula R<sub>3</sub>aluminum<sub>5</sub>O<sub>12</sub> (R is any one sort of rare earth elements among Y, Dy, Ho, Er, Tm, Yb, and Lu), and the pore in a sintered compact is 100 or less volppms, and since the translucency rare earth aluminum garnet sintered compact of this invention is visible, it is crossed to an infrared region and characterized by optical straight-line permeability other than unique absorption wavelength being 83% or more by 5mm thickness. In addition, the amount of pore shall be expressed per volppm and the amount of impurities shall be expressed per wtpm.

[0010] The ratio of rare earth elements and aluminum is 0.599 ≤R/aluminum≤0.601 in mol conversion, the ratio of rare earth

elements and aluminum is  $0.599 \leq R/\text{aluminum} \leq 0.600$ , Si in a sintered compact is 15 or less wtppms, the ratio of rare earth elements and aluminum is  $0.600 < R/\text{aluminum} \leq 0.601$ , and Si in a sintered compact is  $\text{Si}(\text{wtppm}) \leq 15000 \times (R/\text{aluminum}) - 8985$ .

[0011] The manufacture approach of the translucency rare earth aluminum garnet sintered compact of this invention The primary ceramic Plastic solid expressed with general formula  $R_3\text{aluminum}_5\text{O}_{12}$  (R is any one sort of rare earth elements among Y, Dy, Ho, Er, Tm, Yb, and Lu) by which the floc to which specific surface area exceeds 3 micrometers by  $3\text{-}15\text{m}^2/\text{g}$  was produced using 5% or less of raw material powder with the weight fraction is calcinated. the mean particle diameter of 3 micrometers or less, and a theoretical density ratio -- the pore in a sintered compact by 100 or less volppms by making eburation 94% or more and giving isotropic pressure pressurization between heat to this primary sintered compact Since visible, it is characterized by crossing to an infrared region and optical straight-line permeability other than unique absorption wavelength considering as 83% or more of sintered compact by 5mm thickness.

[0012] It is desirable to perform primary baking below 1450 degrees C or more 1700 degrees C. Moreover, 1400-degree-C or more thing which it is 1800 degrees C or less, and is performed by two or less two or more 800 kgf/cm<sup>2</sup>2000 kgf/cm using ambient atmospheres, such as Ar, of HIP is desirable.

[0013]

[An operation and effectiveness] of invention Since pore was 100 or less volppms and this invention person had it, he found out that it crossed to an infrared region and optical straight-line permeability other than unique absorption wavelength could produce 83% or more of rare earth aluminum garnet sintered compact by 5mm thickness. [visible] What is necessary is for that purpose, to calcinate the 1st order to the mean particle diameter of 3 micrometers or less, and 94% or more of theoretical density ratios, and just to give HIP, for example, after fabricating the raw material powder of the sinterable nature which managed the presentation ratio of rare earth elements and aluminum, Si content, primary particle diameter, and the diameter of secondary floc to high density.

[0014] The mole ratio of rare earth elements and aluminum is set to  $0.599 \leq R/\text{aluminum} \leq 0.601$  by mol conversion, and the upper limit content of Si is changed according to this mole ratio. That this mole ratio is a rarefaction region when the range of 0.599-0.601 has low Si concentration, and Si concentration is below an upper limit content are the conditions which prevent formation of the liquid phase in a grain boundary, and this is the conditions for preventing invasion of the gas in HIP processing and preventing generation of pore.

[0015] Pore is removed by accelerating discharge of pore by plastic deformation while calcinating being high pressure and pressurizing a sample isotropic for example, under an elevated temperature and discharging pore with grain growth. To the conventional method having discharged pore only according to the volume spreading effect by grain growth, by this invention, when the plastic deformation effectiveness is also added, it is removable to the pore of unremovable magnitude usual. If  $\text{SiO}_2$ , such as sintering acid, exceed upper limit concentration and exist even if it uses HIP, it will segregate under elevated-temperature high pressure in a grain boundary, Ar of a pressure medium etc. will be hidden, and it will expand by annealing after HIP. For this reason, pore is unremovable.

[0016]

[Example] High grade rare earth aluminum garnet raw material powder is fabricated by the slip casting method.  $R/\text{aluminum}$  sets to  $\text{Si}(\text{ppm}) \leq 15000 \times (R/\text{aluminum}) - 8985$  the amount of Si in the raw material powder used here in 15 ppm or less and  $0.600 < R/\text{aluminum} \leq 0.601$  in  $0.599 \leq R/\text{aluminum} \leq 0.600$ . In any case, the amount of Si makes it 5 ppm or less more preferably.

[0017] when aluminum is more superfluous than stoichiometric, with the aluminum for an excess, Si generates the liquid phase and segregates

it to a grain boundary. Gas, such as Ar, is hidden in the interior of a sintered compact through the segregated grain boundary phase, and sufficient HIP effectiveness stops arising. On the other hand, when rare earth is more superfluous than stoichiometric, with the rare earth elements for an excess, by YAG, Si forms YAP and YAM and localizes them at the triple point of Polycrystal YAG. The critical mass of Si which forms the liquid phase by the overaluminum side is 15 ppm, and in an overyttrium side, since Si is localized at the triple point, the amount of Si which forms the liquid phase in a grain boundary increases in connection with the excessive amount of an yttrium. Therefore, if the amount of Si is restricted, the inflow path of Ar to a grain boundary will not be formed, but the effective HIP effectiveness will produce it.

[0018] A raw material presentation influences the optical property of the sintered compact obtained greatly. The artificer etc. found out extending the rarefaction presentation region of the polycrystalline substance while promoting grain growth, as Si stated previously. In the conventional method, SiO<sub>2</sub> hundreds of ppm or more is added as sintering acid, and a rarefaction presentation region is not so strict. When, as for an artificer etc., 100 ppm of Si exist, it has found out that the rarefaction presentation region of the YAG ceramics is  $0.594 \leq R/\text{aluminum} \leq 0.606$ . However, if the amount of Si is decreased, a rarefaction presentation region will also change, in an Si additive-free case, if it becomes overaluminum from stoichiometric, abnormality grain growth will arise, and if it becomes overrare earth conversely, the unusual appearance from which a refractive index completely differs will arise. Therefore, in order to obtain sufficient transparent body, presentation control is performed more strictly and it is referred to as  $0.599 \leq R/\text{aluminum} \leq 0.601$ .

[0019] In addition, it is satisfactory even if it adds grain growth retardant, such as calcium and Mg, if needed. However, it not only becomes the scattering source of light, but it segregates on the grain community added beyond the need, and it becomes difficult like the case of Si to demonstrate the HIP effectiveness enough. Therefore, as for the addition, it is desirable to be referred to as 80 ppm or less in a stop and the sum total at the need minimal dose. Although the addition approach of these assistants and especially a stage are not limited, it is necessary to add to homogeneity in a Plastic solid.

[0020] While making use raw material powder into sinterable nature and setting specific surface area to 3-15m<sup>2</sup>/g, the secondary floc exceeding 3 micrometers uses 5% or less of raw material of uniform particle size distribution with a weight fraction. Although a degree of sintering becomes good so that a degree of sintering uses impalpable powder depending on the particle diameter of raw material powder, it is not easy specific surface area to carry out eburation at low temperature at below 3m<sup>2</sup>/g. Moreover, in more than 15m<sup>2</sup>/g, it passes in the end of fines, handling is not easy, and it is difficult to make a shaping consistency high. Therefore, specific surface area of a use raw material is set to 3-15m<sup>2</sup>/g from a viewpoint of the ease of a degree of sintering, packing nature, and handling nature. Moreover, it not only prepares specific surface area, but the magnitude of the secondary floc of raw material powder poses a problem. Between the secondary flocs in secondary floc, the big opening set also to several micrometers exists rather than common shaping generates. Since this opening cannot make it disappear in primary baking and HIP processing, the secondary floc exceeding 3 micrometers uses 5% or less of raw material powder with a weight fraction.

[0021] Although any are sufficient as extrusion molding and injection molding which are generally used for manufacture of the ceramics as a fabricating method, press forming, etc., in order to obtain a precise sintered compact with the sufficient yield, a slip casting method is desirable. The magnitude of pore removable [ with HIP ] is below submicron, and it is impossible in primary baking and HIP processing to remove the defect several microns or more produced with poor

packing at the time of shaping. After mixing raw material powder with a lot of binders and considering as the viscous shape of a high compound, in order to fabricate in extrusion molding or injection molding, several micrometers to dozens of micrometers air bubbles tend to enter. Moreover, in order to improve the handling nature of fine particles generally, once using raw material powder as granulation, it fabricates in press forming. Under the present circumstances, it is easy to produce a several micrometers opening on 3 importance formed especially between surrounding granulation between granulation. On the other hand, in a slip casting, that the big defect which also amounts to several micrometers arises is only the case where cast and air bubbles enter during a slip, and such air bubbles can be easily removed by the supersonic wave or the vacuum. Therefore, it is desirable to perform shaping by the slip casting method and to make a shaping consistency 59% or more.

[0022] The acquired Plastic solid performs debinder processing by the pyrolysis. Although the processing temperature in this case, time amount, and an ambient atmosphere change with classes of added shaping assistant, since a debinder will become difficult if a sample forms a closed hole, they are enough performed over many hours below at the temperature from which sintering does not begin. The oxygen ambient atmosphere of an ambient atmosphere is the most common, and performs it under humidification hydrogen, Ar, or reduced pressure if needed.

[0023] The primary sample is calcinated in ambient atmospheres, such as a vacuum, atmospheric air, and hydrogen, after debinder termination, and eburnation is carried out to the mean particle diameter of 3 micrometers or less, and 94% or more of theoretical density ratios. If the mean particle diameter of primary baking objects is too large in the case of HIP processing, since plastic deformation will not arise, removal of pore becomes difficult. In order to crush pore by plastic deformation, it is required for the mean particle diameter of a sample to be 3 micrometers or less, and it is more desirable that it is 1 micrometer or less. Removal of pore is difficult, if eburnation has not been carried out to some extent even when mean particle diameter is 3 micrometers or less. Therefore, it is desirable to carry out eburnation of the primary baking objects to 94% or more of theoretical density, and it is more desirable that it is 96% or more.

[0024] it becomes difficult for the grain growth it it is difficult to fully carry out eburnation, and is too high conversely to advance, and to come out by HIP processing, even when it is any, and to remove pore, if primary burning temperature is too low. Therefore, it calcinates preferably at 1450-degree-C or more temperature of 1700 degrees C or less. For example, when sintering acid is not used and 80 ppm or less of grain growth retardant, such as 1500 degrees C to 1650 degrees C, and calcium, Mg, are added, it is desirable to calcinate in a 1600 to 1700 degrees C temperature requirement. Moreover, since a surface organization will not fully be formed into a closed hole if too short, 30 minutes or more are required for the holding time. When the sample path length is thick, it holds for 2 hours or more, and a front face and the interior are made into homogeneity, but if it is a sample 3mm or less, for example, maintenance of about 1 hour is enough.

[0025] HIP processing is performed in order to remove the pore in the obtained primary sintered compact. Removal of the pore by HIP processing is not based on the plastic deformation under elevated-temperature high pressure, and when processing temperature is low, since mass transfer does not arise, plastic deformation does not happen. Conversely, when processing temperature is too high, in order that a sample may carry out grain growth in the middle of a temperature up, plastic deformation does not happen too. Therefore, HIP temperature has 1400 degrees C or more desirable 1800 degrees C or less, and is desirable. [ of 1550 degrees C - especially 1650 degrees C ] Since grain growth is furthermore promoted for HIP temperature when high [ 100 degrees C or more ] as compared with primary sintering

temperature, and the mechanical strength of the ceramics falls, in order to obtain a high intensity sintered compact, it is desirable to make HIP temperature into the range of  $\sim 50$ -degree C primary sintering temperature.

[0026] It is difficult and it is  $\sim$  to remove pore, when a pressure is insufficient even if selection of a HIP pressure is also important and it optimizes temperature. In order to crush pore at the temperature of 1400 degrees C or more, a two or more 800 kgf/cm pressure is desirable, and when especially the sample path length is 5mm or more, two or more 1000 kgf/cm is desirable. When a HIP pressure exceeds 2000 kgf/cm<sup>2</sup>, maintenance of a high pressure vessel and management are not easy, and there is a problem of dew condensation generating the reduced pressure at the time of cooling in a skillful  $\sim$  trap  $\sim$  pressurized container further, and it is not desirable. Therefore, a HIP pressure has two or less desirable two or more 800 kgf/cm<sup>2</sup> or 2000 kgf/cm.

[0027] [The example 1 of a trial] 15l. of nitric-acid yttrium water solutions of 0.5 mols / L and 25l. of aluminium nitrate water solutions of 0.5 mol/L were mixed, and it considered as the mixed solution of a YAG presentation. Into 40l. of 2 ammonium-carbonate water solutions of M which added aqueous ammonia and were set to pH8.0, this solution was dropped the rate for 1.5l./min. Under the present circumstances, both the mixed solutions and ammonium-hydrogencarbonate water solutions of a YAG presentation were maintained at 30 degrees C. The minimum value of pH in the middle of dropping is 7.0, and pH amounted to 7.8 of constant value in about 3 hours after dropping termination. After dropping termination and after recuperating oneself at 30 degrees C for 48 hours, filtration and rinsing were repeated 6 times and the YAG precursor was obtained. In all the precursor production processes, ultrapure water (conductivity 18 M  $\Omega$ -cm) was used.

[0028] Temporary quenching of the obtained YAG precursor was carried out at 1300 degrees C among atmospheric air for 5 hours, and the YAG raw material powder of 0.4 micrometers of diameters of a primary particle was produced. Purity analysis of raw material powder was performed using ICP, and it became clear that it was 99.95% or more of purity, and the mole ratio of Si of 3 ppm and Y/aluminum was 0.600. Moreover, the weight fraction exceeding 3 micrometers of floc was 1% or less.

[0029] 4.2g of FUREN G-700 made from the Kyoeisha chemistry was added to 200g of obtained YAG raw material powder as a deflocculant, 1g of Sekisui Chemical PVB-BL1 was further added to it as a binder, ethanol 50g was added to it, and it mixed for 12 hours using the nylon pot and the nylon ball, and considered as the alcoholic slurry. This slurry was slushed into the plaster mold and the 50mmx50mmx10mm Plastic solid was acquired. The temperature up of this Plastic solid was carried out by 10 degrees C/hr among the oxygen air current, it was degreased at 750 degrees C among oxygen for 100 hours, and the Plastic solid consistency after cleaning processing was 60.7%. Next, the 1st order of this Plastic solid was calcinated at the temperature of 1500 degrees C with the vacuum furnace for 2 hours. Under the present circumstances, the programming rate was set to 400 degrees C / hr, and the pressure was set to 10 to 3 or less Torrs. the theoretical density ratio of primary baking objects -- Archimedes -- it was 96.4% as a result of asking by law. Moreover, as a result of observing the microstructure inside a sintered compact with an optical microscope, sintered compact mean particle diameter was 1.2 micrometers.

[0030] The temperature up of this primary baking object was carried out to 1550 degrees C by 500 degrees C/hr, and HIP was performed by the pressure of 1250 kgf/cm<sup>2</sup> in Ar for 2 hours. From the obtained sintered compact, mirror polishing of ten-sheet logging both sides was carried out for the sample of 40x8x0.5mm of abbreviation by the diamond slurry, and the pore in [ all ] a sample was observed using the transparency microscope. The amount of pore was 7volppm(s), as a result of observing the number of pores, and a pore diameter and



carrying out volume conversion. Moreover, after starting to 5.0mm thickness and carrying out mirror polishing of both sides, as a result of measuring straight-line permeability with a spectrophotometer, it was 84% on the wavelength of 500nm.

[0031]

[The examples 2-9 of a trial] SiO<sub>2</sub> was added to the high grade RUTCHUUMUARU minium garnet (it abbreviates to Lu<sub>3</sub>aluminum<sub>5012</sub>:LuAG) raw material powder produced like the example 1 of a trial, and the sintered compact was produced like the example 1 of a trial (examples 2-9 of a trial). The relation of the amount of Si and porosity in a sintered compact is shown in Table 1. In addition, the mole ratio of Lu of this sample and aluminum was Lu/aluminum=0.599. Table 1 shows that it is necessary to set Si in a sintered compact to 15 ppm or less, in order to set the porosity in a sintered compact to 100 or less volppms.

[0032]

[Table 1]

Si in a sintered compact, and the relation of porosity Si/ppm Porosity/volppm The example 2 of an optical straight-line permeability (500nm / 5mm thickness) trial 3 3 The example 3 of 84 trials 8 43 Example 4 of 84 trials 14 72 Example 5 of 83 trials 17 110 Example 6 of 80 trials 22 240 Example 7 of 77 trials 50 600 Example 8 of 72 trials 120950 Example 9 of 65 trials 500 1350 60 [0033]

[The examples 10-14 of a trial] The high grade LuAG raw material powder with which presentations differ was produced like the example 1 of a trial, SiO<sub>2</sub> was added and the sintered compact was produced like the example 1 of a trial. The relation between the presentation of a sintered compact, Si content, and porosity is shown in Table 2. In the case of Lu/aluminum=0.601, it is from Table 2. Although Si is [ porosity ] 100 or less volppms, 30 ppm is known by that porosity increases rapidly when Si becomes more than it. Moreover, even when there are few amounts of Si than the examples 13 and 14 of a trial, it turns out that pore cannot remove a slight presentation gap enough, either.

[0034]

[Table 2]

The examples 10-14 of a trial Lu/aluminum Si/ppm Porosity / example 10 of a volppm trial 0.601 3 Example 11 of 3 trials 0.601 28 Example 12 of 81 trials 0.601 35 Example 13 of 270 trials 0.598 3 Example 14 of 1400 trials 0.603 3 220 [0035]

[The examples 15-24 of a trial] the high grade ITTERRUBIUMU aluminum garnet (it abbreviates to Yb<sub>3</sub>aluminum<sub>5012</sub>:YbAG) precursor was produced like the example 1 of a trial, various the temperature and time amount at the time of temporary quenching were boiled and changed, and the high grade YbAG raw material powder with which primary particle diameter differs from a condensation degree was produced. The raw material presentation was R/aluminum=0.600, as a result of ICP's performing purity analysis, in all cases, the purity was 99.95% or more, and Si was 3 ppm or less. After producing the Plastic solid like the example 1 of a trial and performing debinder processing using these raw material powder, primary baking was performed so that it might become the average crystal particle diameter of 3 micrometers or less, and 94% or more of theoretical density ratios at 1575 degrees C with a vacuum furnace. HIP was given for this primary sintered compact at 2000 kgf/cm<sup>2</sup> in Ar, and 1600 degrees C. The BET surface area value of raw material powder, the weight fraction of floc 3 micrometers or more, and the porosity contained inside the obtained sintered compact are shown in Table 3. The examples 15-19 of a trial show that porosity increases it depending on the weight fraction of the floc 3 micrometers or more in start raw material powder, so that the porosity of a sintered compact has many the rates.

[0036]

[Table 3]

The examples 15-24 of a trial BET (cm<sup>2</sup>/g) 3-micrometer or more floc (wt%) The example 15 of a porosity (ppm) trial 3.44.1 The example 16

of 57 trials 5.8 2.2 The example 17 of 21 trials 8.4 1.0 Example 18 of 3 trials 11.0 3.3 Example 19 of 9 trials 14.6 4.6 The example 20 of 34 trials 2.7 4.6 The example 21 of 110 trials 3.5 6.2 Example 22 of 185 trials 6.8 10.8 Example 23 of 630 trials 12.3 8.5 Example 24 of 565 trials 16.74.8 250 [0037] Like the example 1 of a trial, various rare earth aluminum garnet sintered compacts were produced, and the three-point flexural strength in a room temperature was measured based on JIS1601. Baking conditions, porosity, three-point flexural strength, and weibull modulus are shown in the following table. The thing which has low porosity showed high reinforcement, and, in all cases, three-point flexural strength was 350 or more MPas.

[0038]

[Table 4]

Porosity and three-point flexural strength of various materials  
Material Primary baking HIP temperature Pressure Porosity Three-point  
flexural strength weibull modulus (degree-Cxhr) (degree-Cxhr)  
(kgf/cm<sup>2</sup>) (ppm) (MPa) Y3aluminum 5012 1550x2 1550x2 1250 7 430  
7D(ies)3aluminum 5012 1500x2 1525x3 1500 25 410 6Ho(es)3aluminum 5012  
1550x21600x31000 68 365 7Er(s)3aluminum 5012 1600x3 1650x2 800 92 350  
6Tm3aluminum 5012 1650x51700x5 1800 35 395 7Yb3aluminum 5012 1575x3  
1600x2 800 50 380 7Lu3aluminum 5012 1525x3 1550x2 1250 3 450 8 [0039]

Table 1 - 4 shows that that porosity is 100 ppm or less are the conditions which make straight-line permeability 83% or more by the sample of 5mm thickness by 500nm. And Si makes porosity increase and it turns out that it differs by whether overrare earth and the aluminum of the relation between porosity and Si concentration are superfluous. Furthermore, porosity is made to increase, the BET surface area of a start raw material has desirable 3-15m<sup>2</sup>/g, and the increment in porosity understands that the floc 3 micrometers or more in a start raw material is not desirable, either also in respect of a mechanical strength required for a high-pressure electric-discharge lamp etc.

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最終頁に続く

(54) 【発明の名称】 透光性希土類アルミニウムガーネット焼結体及びその製造方法

(57) 【要約】

【構成】 焼結体中の気孔が100volppm以下、モル換算で希土類元素とアルミニウムとの比が $0.599 \leq R/AI \leq 0.601$ であり、 $0.599 \leq R/AI \leq 0.600$ ではSiが15wtppm以下で、 $0.600 < R/AI \leq 0.601$ ではSi (wtppm)  $\leq 15000 \times (R/AI) - 8985$ である透光性希土類アルミニウムガーネット焼結体。

【効果】 光直線透過率が高く、また機械的強度に優れている。

## 【特許請求の範囲】

【請求項1】 結晶構造が一般式 $R_3Al_5O_{12}$ （ $R$ は $Y$ 、 $Dy$ 、 $Ho$ 、 $Er$ 、 $Tm$ 、 $Yb$ 、 $Lu$ のうちいずれか1種の希土類元素）で表されるガーネット構造を有する焼結体であって、焼結体中の気孔が100volppm以下で、かつ可視から赤外領域に渡って特異吸収波長以外での光直線透過率が5mm厚みで83%以上であることを特徴とする透光性希土類アルミニウムガーネット焼結体。

【請求項2】 モル換算で希土類元素とアルミニウムとの比が $0.599 \leq R/Al \leq 0.601$ であり、希土類元素とアルミニウムとの比が $0.599 \leq R/Al \leq 0.600$ で、焼結体中の $Si$ が15wtppm以下であり、希土類元素とアルミニウムとの比が $0.600 < R/Al \leq 0.601$ で、焼結体中の $Si$ が $Si$  (wtppm)  $\leq 15000 \times (R/Al) - 8985$ である、ことを特徴とする請求項1の透光性希土類アルミニウムガーネット焼結体。

【請求項3】 比表面積が $3 \sim 15 m^2/g$ で、 $3 \mu m$ を超える凝集粒子が重量分率で5%以下の原料粉末を用いて作製された一般式 $R_3Al_5O_{12}$ （ $R$ は $Y$ 、 $Dy$ 、 $Ho$ 、 $Er$ 、 $Tm$ 、 $Yb$ 、 $Lu$ のうちいずれか1種の希土類元素）で表されるセラミックス成形体を1次焼成して、平均粒径 $3 \mu m$ 以下、理論密度比94%以上に緻密化し、この1次焼結体に熱間等方圧加圧を施すことにより、焼結体中の気孔が100volppm以下で、可視から赤外領域に渡って特異吸収波長以外での光直線透過率が5mm厚みで83%以上の焼結体とすることを特徴とする、透光性希土類アルミニウムガーネット焼結体の製造方法。

## 【発明の詳細な説明】

## 【0001】

【発明の利用分野】 本発明は、一般式 $R_3Al_5O_{12}$ （ $R$ は $Y$ 、 $Dy$ 、 $Ho$ 、 $Er$ 、 $Tm$ 、 $Yb$ 、 $Lu$ のうちいずれか1種の希土類元素）で表されるガーネット構造を有する、透光性焼結体及びその製造方法に関する。本発明の焼結体は、例えばサファイヤ代替窓材、偏光板、放電ランプ用エンベロープ、半導体製造装置等の耐食部材、装飾品等に好適に用いられる。

## 【0002】

【従来技術】 一般式 $R_3Al_5O_{12}$ （ $R$ は $Y$ 、 $Dy$ 、 $Ho$ 、 $Er$ 、 $Tm$ 、 $Yb$ 、 $Lu$ のうちいずれか1種の希土類元素）で表される希土類アルミニウムガーネット化合物は、その結晶構造が立方晶であり、透光性や耐熱性に優れた焼結体を得られるため、様々な用途への適用ができる。特に、光の散乱源である気孔や異相を完全に除去することにより、多結晶体でありながら単結晶に匹敵する透明度が得られるため、各種光学材料への適用が期待されている。

【0003】 中でもイットリウムアルミニウムガーネッ

ト（ $Y_3Al_5O_{12}$ ：YAG）セラミックスは可視部から赤外領域までの広範囲に渡り優れた透光性を示すため、セラミックスの利点である強度、耐熱性及び形状自由度を期待して、サファイヤ代替窓材、放電ランプ用発光管材料、耐食部材等への適用が検討されている。一方、イットリウム以外の希土類元素を用いた透光性希土類アルミニウムガーネット焼結体は、希土類元素が比較的高価であること、さらに特定の用途が見出せないことから、製造条件がYAGセラミックスの場合とほぼ同様であるにもかかわらず、製造方法に関する報告はほとんど見当たらない。

【0004】 従来より盛んに研究が行われている透光性YAGセラミックスの製造方法として、ホットプレス法によるもの（米国特許：3767, 745）や、酸化物微粉末のボールミル混合・CIP成形による直接焼結法（特開平3-218963号）等が知られている。ホットプレス法は、セラミックスの特徴の1つである複雑形状品の製造を困難にする。酸化物微粉末混合法では、透光性の良い焼結体を得られるものの、反応性を増すと共に混合時の比重差に基づくイットリアとアルミナの分離を抑制するため、イットリアの超微粉末を用いる。このため、イットリアとアルミナを別々に製造する必要がある上、超微粉末を用いるため、成形密度が低くなる傾向がある。成形密度が低いと、焼結時の収縮が大きく、寸法精度が要求される用途には適用が困難である。さらに十分な透光性を示す焼結体を得るためには、焼結助剤として $SiO_2$ を添加し、数十時間焼成を行う必要がある。また単一相YAG微粉末を用いて透光性焼結体を得る方法（特開平2-92817号）も開示されているが、原料粉末の焼結性が乏しいことから、 $SiO_2$ 等の焼結助剤を必要とする。

【0005】 一般に結晶構造が立方晶からなるセラミックス中の光の散乱源は、気孔及び異相であり、透光性に優れた焼結体を得るには、これらを完全に除去する必要がある。希土類アルミニウムガーネット焼結体の様な2成分系の酸化物では、組成を厳密に制御することにより、異相の発生を抑制できる。気孔の存在は、透光性を低下させるのみならず、破壊源とも成り得るため好ましくない。従って透光性に優れ、また機械的にも信頼性の高い焼結体を得るには、気孔を如何に除去するかが課題となる。

【0006】 従来法では、焼結助剤及び焼成条件により緻密化及び粒成長速度を制御し、粒成長による体積拡散により結晶粒界を通して気孔の排出を行っている。しかしながら、通常の原料粉末ならびに機械成形法を用いたセラミックスの製造では、原料粒子の均一なパッキングは不可能であり、多かれ少なかれ通常の焼結では取り除けない大きさの空孔が生じる。従って、一般的に緻密体といわれている透光性セラミックスでも、焼結体内部には数100volppm以上の気孔が残存しており、単結晶と

同一の光学特性を示す多結晶体を得ることは困難である。例えばジャーナルオブマテリアルサイエンス (Journal of Materials Science) 34(1999)1189-1195では、真空焼結法により得られたNd添加YAGセラミックス内部に気孔は最低でも150volppm存在していると報告し、この値は単結晶のそれと比較して極めて多い。

【0007】ところで、透光性アルミナの作製では熱間等方圧加圧 (Hot Isostatic Press:HIP)により、気孔を含まない焼結体を得られることが開示されている (特開平8-301666号)。HIPでは、高温下にて試料に数百kgf/cm<sup>2</sup>以上の高圧を等方的に加え、塑性変形によってセラミックス内の気孔を除去する。一方YAGセラミックスにHIPを適用し、無気孔焼結体を作製しようとした例として、ジャーナルオブアメリカンセラミックスソサエティ (J. Am. Ceram. Soc) 79[7] 1927-33(1996)が報告されている。しかしながらこの報告では、圧力媒体であるArガスが焼結体内部に気孔として残存するため、無気孔YAG焼結体を作製することは不可能であるとされている。以上に述べたように、従来法ではYAGをはじめとする希土類アルミニウムガーネットの無気孔焼結体は、知られていない。

【0008】

【発明の課題】本発明の目的は、光透過率に優れた希土類アルミニウムガーネット焼結体、及びその製造方法を提供することにある。

【0009】

【発明の構成】本発明の透光性希土類アルミニウムガーネット焼結体は、結晶構造が一般式R<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> (RはY, Dy, Ho, Er, Tm, Yb, Luのうちいずれか1種の希土類元素) で表されるガーネット構造を有する焼結体であって、焼結体中の気孔が100volppm以下で、かつ可視から赤外領域に渡って特異吸収波長以外での光直線透過率が5mm厚みで83%以上であることを特徴とする。なお気孔の量はvolppm単位で表し、不純物量はwtppm単位で表すものとする。

【0010】モル換算で希土類元素とアルミニウムとの比が $0.599 \leq R/Al \leq 0.601$ であり、希土類元素とアルミニウムとの比が $0.599 \leq R/Al \leq 0.600$ で、焼結体中のSiが15wtppm以下であり、希土類元素とアルミニウムとの比が $0.600 < R/Al \leq 0.601$ で、焼結体中のSiが $Si(wtppm) \leq 15000 \times (R/Al) - 8985$ である。

【0011】本発明の透光性希土類アルミニウムガーネット焼結体の製造方法は、比表面積が3~15m<sup>2</sup>/gで、3μmを超える凝集粒子が重量分率で5%以下の原料粉末を用いて作製された一般式R<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> (RはY, Dy, Ho, Er, Tm, Yb, Luのうちいずれか1種の希土類元素) で表されるセラミックス成形体を1次焼成して、平均粒径3μm以下、理論密度比94%以上に緻密化し、この1次焼結体に熱間等方圧加圧を施

すことにより、焼結体中の気孔が100volppm以下で、可視から赤外領域に渡って特異吸収波長以外での光直線透過率が5mm厚みで83%以上の焼結体とすることを特徴とする。

【0012】1次焼成は1450℃以上1700℃以下で行うことが好ましい。またHIPは、1400℃以上1800℃以下で、Ar等の雰囲気を用いて、800kgf/cm<sup>2</sup>以上2000kgf/cm<sup>2</sup>以下で行うことが好ましい。

【0013】

【発明の作用と効果】本発明者は、気孔が100volppm以下であって可視から赤外領域に渡って特異吸収波長以外での光直線透過率が5mm厚みで83%以上の希土類アルミニウムガーネット焼結体を作製できることを見出した。そのためには例えば、希土類元素とアルミニウムとの組成比、Si含有量、1次粒子径及び2次凝集粒子径を管理した易焼結性の原料粉末を高密度に成形した後、平均粒子径3μm以下、理論密度比94%以上に1次焼成し、HIPを施せば良い。

【0014】モル換算で希土類元素とアルミニウムとのモル比を $0.599 \leq R/Al \leq 0.601$ とし、Siの上限含有量はこのモル比に応じて変化させる。このモル比が $0.599 \sim 0.601$ の範囲がSi濃度が低い際の透明化域であり、Si濃度が上限含有量以下であることが、粒界での液相の形成を防止する条件であり、このことはHIP処理でのガスの侵入を防止して、気孔の生成を阻止するための条件である。

【0015】気孔は、例えば高温下において試料を高圧で等方的に加圧しながら焼成して、粒成長により気孔を排出すると共に、塑性変形により気孔の排出を加速することにより除去する。従来法が粒成長による体積拡散効果のみによって気孔を排出しているのに対し、本発明では塑性変形効果も加わる事により、通常では除去不可能な大きさの気孔まで除去できる。HIPを用いても、焼結助剤等のSiO<sub>2</sub>が上限濃度を超過して存在すると、高温高圧下において粒界に偏析し、圧力媒体のAr等が潜り込み、HIP後のアニールによって膨張する。このため気孔は除去できない。

【0016】

【実施例】高純度希土類アルミニウムガーネット原料粉末を、鋳込み成形法により成形する。ここで使用する原料粉末中のSi量は $R/Al$ が $0.599 \leq R/Al \leq 0.600$ の範囲では15ppm以下、 $0.600 < R/Al \leq 0.601$ の範囲では $Si(ppm) \leq 15000 \times (R/Al) - 8985$ とする。いずれの場合も、Si量はより好ましくは5ppm以下とする。

【0017】正規組成よりもアルミニウム過剰の場合、Siは過剰分のアルミニウムと共に液相を生成し粒界に偏析する。偏析した粒界相を通してAr等のガスが焼結体内部に潜り込み充分なHIP効果が生じなくなる。これに対して正規組成よりも希土類過剰の場合、Siは過

剰分の希土類元素と共に、例えばYAGではYAPやYAMを形成し、多結晶YAGの三重点に局在化する。アルミニウム過剰側で液相を形成するSiの限界量は15ppmで、イットリウム過剰側では三重点にSiが局在化されるため、粒界に液相を形成するSi量はイットリウムの過剰量に伴い増加する。従ってSi量を制限すれば、粒界へのArの流入経路は形成されず、有効なHIP効果が生じる。

【0018】原料組成は、得られる焼結体の光学特性を大きく左右する。発明者等は、Siが先に述べたように、粒成長を促進すると共に、多結晶体の透明化組成域を広げることを見出した。従来法では、焼結助剤としてSiO<sub>2</sub>を数百ppm以上添加しており、透明化組成域はそれほど厳密ではない。発明者等は、Siが100ppm存在する場合、YAGセラミックスの透明化組成域は $0.594 \leq R/AI \leq 0.606$ であることを見出している。しかしながらSi量を減少させると、透明化組成域も変化し、Si無添加の場合、正規組成よりもアルミニウム過剰になると異常粒成長が生じ、逆に希土類過剰になると屈折率の全く異なる異相が生じる。従って充分な透明体を得るために、より厳密に組成制御を行い、 $0.599 \leq R/AI \leq 0.601$ とする。

【0019】なお必要に応じ、Ca、Mg等の粒成長抑制剤を添加しても問題ない。但し、必要以上に添加すると粒界に偏析し、光の散乱源となるのみならず、Siの場合と同様、HIP効果を充分発揮することが困難となる。従ってその添加量は必要最小量に止め、合計で80ppm以下とすることが好ましい。これら助剤の添加方法及び時期は特に限定するものではないが、成形体中に均一に添加する必要がある。

【0020】使用原料粉末は易焼結性とし、比表面積を $3 \sim 15 \text{ m}^2/\text{g}$ とすると共に、 $3 \mu\text{m}$ を超える2次凝集粒子が重量分率で5%以下の、均一な粒度分布の原料を使用する。焼結性は原料粉末の粒子径に依存し、微粉末を使用するほど焼結性は良くなるが、比表面積が $3 \text{ m}^2/\text{g}$ 以下では、低温で緻密化させることは容易でない。また $15 \text{ m}^2/\text{g}$ 以上の場合には微粉末過ぎて、ハンドリングが容易ではなく、成形密度を高くすることは困難である。従って、焼結性、パッキング性及びハンドリング性の容易さの観点から、使用原料の比表面積は $3 \sim 15 \text{ m}^2/\text{g}$ とする。また比表面積を調製するだけでなく、原料粉末の2次凝集粒子の大きさも問題となる。2次凝集粒子内ないし2次凝集粒子間には、一般の成形によって生成するよりも大きな、数 $\mu\text{m}$ にもなる空隙が存在する。この空隙は1次焼成及びHIP処理では消滅させることが出来なため、 $3 \mu\text{m}$ を超える2次凝集粒子が重量分率で5%以下の原料粉末を用いる。

【0021】成形法としては、セラミックスの製造に一般に用いられている押出し成形、射出成形、プレス成形等いずれでも良いが、歩留まり良く緻密な焼結体を得る

ため鑄込み成形法が好ましい。HIPにより除去可能な気孔の大きさはサブミクロン以下であり、成形時のパッキング不良により生じた数ミクロン以上の欠陥を除去することは、1次焼成及びHIP処理では不可能である。押出し成形や射出成形では、原料粉末を大量のバインダーと混合し、粘性の高いコンパウンド状とした後、成形するため、数 $\mu\text{m}$ から数十 $\mu\text{m}$ の気泡が入りやすい。またプレス成形では、一般に粉体のハンドリング性を改善するため、一旦原料粉末を顆粒とした後、成形する。この際、顆粒間、特に周辺の顆粒との間で形成される3重点に、数 $\mu\text{m}$ の空隙が生じやすい。これに対して鑄込み成形では、数 $\mu\text{m}$ にも及ぶ大きな欠陥が生じるのは鑄込みスリップ中に気泡が入った場合のみであり、このような気泡は超音波や真空により簡単に取り除くことができる。従って成形は鑄込み成形法で行い、成形密度を59%以上にしておくのが好ましい。

【0022】得られた成形体は、熱分解による脱バインダー処理を行う。この際の処理温度、時間、雰囲気は、添加した成形助剤の種類により異なるが、試料が閉空孔化してしまうと脱バインダーが困難となるため、焼結の始まらない温度以下で充分時間をかけて行う。雰囲気は酸素雰囲気が最も一般的で、必要に応じ加湿水素やAr、もしくは減圧下で行う。

【0023】脱バインダー終了後、試料を真空、大気、水素等の雰囲気中で1次焼成し、平均粒径 $3 \mu\text{m}$ 以下、理論密度比94%以上に緻密化させる。HIP処理の際、1次焼成体の平均粒子径が大きすぎると、塑性変形が生じないため、気孔の除去が困難となる。塑性変形により気孔を押し潰すためには、試料の平均粒径が $3 \mu\text{m}$ 以下であることが必要で、 $1 \mu\text{m}$ 以下であることがより好ましい。平均粒径が $3 \mu\text{m}$ 以下の場合でも、ある程度緻密化していないと、気孔の除去が難しい。従って1次焼成体を理論密度の94%以上まで緻密化させるのが好ましく、96%以上であることがより好ましい。

【0024】1次焼成温度が低すぎると、充分に緻密化させることが困難であり、逆に高すぎると粒成長が進行し、いずれの場合でもHIP処理により気孔を除去することが困難となる。従って、好ましくは $1450^\circ\text{C}$ 以上 $1700^\circ\text{C}$ 以下の温度で焼成を行う。例えば焼結助剤を用いない場合には $1500^\circ\text{C}$ から $1650^\circ\text{C}$ 、Ca、Mg等の粒成長抑制剤を80ppm以下添加した場合には $1600^\circ\text{C}$ から $1700^\circ\text{C}$ の温度範囲で焼成することが好ましい。また保持時間は、短すぎると表面組織が充分に閉空孔化されないため、30分以上が必要である。試料厚みが厚い場合には2時間以上保持し、表面と内部を均一にするが、例えば3mm以下の試料であれば1時間程度の保持で充分である。

【0025】得られた1次焼結体中の気孔を除去するために、HIP処理を行う。HIP処理による気孔の除去は、高温高圧下での塑性変形によるものであり、処理温

度が低い場合、物質移動が生じないため塑性変形は起こらない。逆に処理温度が高すぎる場合、昇温途中に試料が粒成長してしまうため、やはり塑性変形は起こらない。従ってHIP温度は1400℃以上1800℃以下が好ましく、1550℃～1650℃が特に好ましい。さらにHIP温度が一次焼結温度と比較して100℃以上高い場合、粒成長が促進され、セラミックスの機械的強度が低下するため、高強度焼結体を得るには、HIP温度を一次焼結温度±50℃の範囲とすることが好ましい。

【0026】HIP圧力の選定も重要であり、温度の最適化を行っても圧力不足の場合には、気孔を除去することは困難である。1400℃以上の温度で気孔を押し潰すためには、800kgf/cm<sup>2</sup>以上の圧力が好ましく、特に試料厚みが5mm以上の場合、1000kgf/cm<sup>2</sup>以上が好ましい。HIP圧力が2000kgf/cm<sup>2</sup>を超える場合、高圧容器の維持、管理が容易ではなく、さらに冷却時の減圧を上手く行わなければ圧力容器内に結露が発生する等の問題があり、好ましくない。従って、HIP圧力は800kgf/cm<sup>2</sup>以上2000kgf/cm<sup>2</sup>以下が好ましい。

#### 【0027】

【試験例1】0.5mol/Lの硝酸イットリウム水溶液15リッターと0.5mol/Lの硝酸アルミニウム水溶液25リッターを混合し、YAG組成の混合溶液とした。アンモニア水を加えてpH8.0とした2Mの炭酸アンモニウム水溶液40リッター中に、この溶液を1.5リッター／分の速度で滴下した。この際、YAG組成の混合溶液と、炭酸水素アンモニウム水溶液は共に30℃に維持した。滴下の途中でのpHの最小値は7.0で、滴下終了後3時間程度でpHは一定値の7.8に達した。滴下終了後、30℃で48時間養生した後、濾過、水洗を6回繰り返し、YAG前駆体を得た。前駆体製造工程の全てにおいて超純水（導電率18MΩ・cm）を使用した。

【0028】得られたYAG前駆体を大気中1300℃で5時間仮焼し、一次粒子径0.4μmのYAG原料粉末を作製した。ICPを用いて原料粉末の純度分析を行い、純度99.95%以上、Siは3ppm、Y／Alのモル比は0.600であることが判明した。また3μmを超える凝集粒子の重量分率は1%以下であった。

#### 焼結体中のSiと気孔率の関係

	Si / ppm	気孔率 / volppm	光直線透過率 (500nm / 5mm厚)
試験例2	3	3	84
試験例3	8	43	84
試験例4	14	72	83
試験例5	17	110	80
試験例6	22	240	77
試験例7	50	600	72
試験例8	120	950	65
試験例9	500	1350	60

【0029】得られたYAG原料粉末200gに、解膠剤として共栄社化学製フローレンG-700を4.2g添加し、さらにバインダーとして積水化学製PVB-BL1を1g添加して、エタノール50gを加え、ナイロンボット及びナイロンボールを用いて12時間混合し、アルコールスラリーとした。このスラリーを石膏型に流し込み、50mm×50mm×10mmの成形体を得た。この成形体を、酸素気流中10℃／hrで昇温し、酸素中750℃で100時間脱脂し、脱脂処理後の成形体密度は60.7%であった。次にこの成形体を、真空炉で1500℃の温度で2時間1次焼成した。この際、昇温速度は400℃／hr、圧力は10<sup>-3</sup>Torr以下とした。1次焼成体の理論密度比をアルキメデス法により求めた結果、96.4%であった。また焼結体内部の微構造を光学顕微鏡で観察した結果、焼結体平均粒子径は1.2μmであった。

【0030】この1次焼成体を、500℃／hrで1550℃まで昇温し、Ar中1250kgf/cm<sup>2</sup>の圧力で2時間HIPを行った。得られた焼結体から、略40×8×0.5mmの試料を10枚切り出し両面をダイヤモンドスラリーで鏡面研磨し、透過顕微鏡を用いて全試料中の気孔を観察した。気孔数ならびに気孔径を観察し体積換算した結果、気孔の量は7volppmであった。また、5.0mm厚に切り出し両面を鏡面研磨したのち分光光度計で直線透過率を測定した結果、波長500nmで84%であった。

#### 【0031】

【試験例2～9】試験例1と同様にして作製した高純度ルテチウムアルミニウムガーネット（Lu<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>：LuAGと略す）原料粉末にSiO<sub>2</sub>を添加し、試験例1と同様にして焼結体を作製した（試験例2～9）。焼結体中のSi量と気孔率の関係を表1に示す。なおこの試料のLuとアルミニウムとのモル比はLu／Al＝0.599であった。表1から、焼結体中の気孔率を100volppm以下にするためには、焼結体中のSiを15ppm以下にする必要があることが判る。

#### 【0032】

##### 【表1】

## 【0033】

【試験例10～14】試験例1と同様にして、組成の異なる高純度LuAG原料粉末を作製し、SiO<sub>2</sub>を添加し、試験例1と同様にして焼結体を作製した。焼結体の組成、Si含有量及び気孔率の関係を表2に示す。表2より、Lu/Al=0.601の場合、Siが30ppm

試験例10～14

	Lu/Al	Si/ppm	気孔率/volppm
試験例10	0.601	3	3
試験例11	0.601	28	81
試験例12	0.601	35	270
試験例13	0.598	3	1400
試験例14	0.603	3	220

## 【0035】

【試験例15～24】試験例1と同様にして高純度イットリウムアルミニウムガーネット（Yb3Al5O12：YbAGと略す）前駆体を作製し、仮焼時の温度及び時間を種々に変更して、1次粒子径及び凝集度合いの異なる高純度YbAG原料粉末を作製した。原料組成はR/Al=0.600であり、ICPにより純度分析を行った結果、全ての場合においてその純度は99.95%以上、Siは3ppm以下であった。これら原料粉末を用い、試験例1と同様にして成形体を作製し、脱バインダー処理を行った後に、真空炉で1575℃で平均結晶粒

試験例15～24

	BET (cm <sup>2</sup> /g)	3μm以上凝集粒子(wt%)	気孔率(ppm)
試験例15	3.4	4.1	57
試験例16	5.8	2.2	21
試験例17	8.4	1.0	3
試験例18	11.0	3.3	9
試験例19	14.6	4.6	34
試験例20	2.7	4.6	110
試験例21	3.5	6.2	185
試験例22	6.8	10.8	630
試験例23	12.3	8.5	565
試験例24	16.7	4.8	250

【0037】試験例1と同様にして、各種希土類アルミニウムガーネット焼結体を作製し、JIS1601に基づき室温での3点曲げ強度を測定した。焼成条件と気孔率、3点曲げ強度及びワイル係数を下表に示す。気孔

各種素材の気孔率と3点曲げ強度

素材	1次焼成 (℃×hr)	HIP温度 (℃×hr)	圧力 (kgf/cm <sup>2</sup> )	気孔率 (ppm)	3点曲げ強度 (MPa)	ワイル係数
Y3Al5O12	1550×2	1550×2	1250	7	430	7

までは気孔率が100volppm以下であるが、Siがそれ以上になると急激に気孔率が増加することが判る。また試験例13、14より、Si量が少ない場合でも、僅かの組成ずれでも気孔が充分除去できないことが判る。

## 【0034】

## 【表2】

子径3μm以下、理論密度比94%以上となるように一次焼成を行った。この1次焼結体をAr中2000kgf/cm<sup>2</sup>、1600℃でHIPを施した。原料粉末のBET表面積値、3μm以上の凝集粒子の重量分率、及び得られた焼結体内部に含まれる気孔率を表3に示す。試験例15～19により、焼結体の気孔率は出発原料粉末中の3μm以上の凝集粒子の重量分率に依存し、その割合が多いほど気孔率が増加することが判る。

## 【0036】

## 【表3】

率の低いもののほど高い強度を示しており、全ての場合において3点曲げ強度は350MPa以上であった。

## 【0038】

## 【表4】



Dy3Al5O12	1500×2	1525×3	1500	25	410	6
Ho3Al5O12	1550×2	1600×3	1000	68	365	7
Er3Al5O12	1600×3	1650×2	800	92	350	6
Tm3Al5O12	1650×5	1700×5	1800	35	395	7
Yb3Al5O12	1575×3	1600×2	800	50	380	7
Lu3Al5O12	1525×3	1550×2	1250	3	450	8

【0039】表1～表4から、気孔率が100ppm以下であることが、500nmで5mm厚の試料で、直線透過率を83%以上とする条件であることが判る。そしてSiは気孔率を増加させ、気孔率とSi濃度の関係は希土類過剰かアルミニウム過剰かで異なることが判る。さら

に、出発原料中の3μm以上の凝集粒子も気孔率を増加させ、出発原料のBET表面積は3～15m<sup>2</sup>/gが好ましく、気孔率の増加は高圧放電灯等に必要な機械的強度の点でも好ましくないことが判る。

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